Preparation of tetrahydrogeranylacetone

The present invention relates to a process for preparing
5 tetrahydrogeranylacetone by selectively hydrogenating
pseudoionone, geranylacetone and/or dihydrogeranylacetone.

Tetrahydrogeranylacetone (THGAC, hexahydropseudoionone) is used
as a starting material for preparing isophytol which for its part
10 is used as a reactant for preparing vitamin E and vitamin K (see,
for example, Ullmann's Encyclopedia of Industrial Chemistry, 5th
ed. on CD-Rom, "Vitamins", chapter 4.11).

GB 788,301 describes a process for preparing THGAC in which
15 geranylacetone or dihydrogeranylacetone (tetrahydropseudoionone)
is hydrogenated in the last step to THGAC.

In principle, THGAC should also be accessible by hydrogenating
pseudoionone which may be prepared by reacting citral with
20 acetone or by reacting dihydrolinalool with diketene or with
isopropenyl methyl ether (see Ullmann's Encyclopedia of
Industrial Chemistry, loc cit.). However, when preparing THGAC
from pseudoionone, the problem occurs that three olefinic double
bonds have to be selectively hydrogenated in the presence of a
25 ketocarbonyl group (see scheme 1).

Scheme 1

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pseudoionone

THGAC

6,10-dimethylundecan-2-ol

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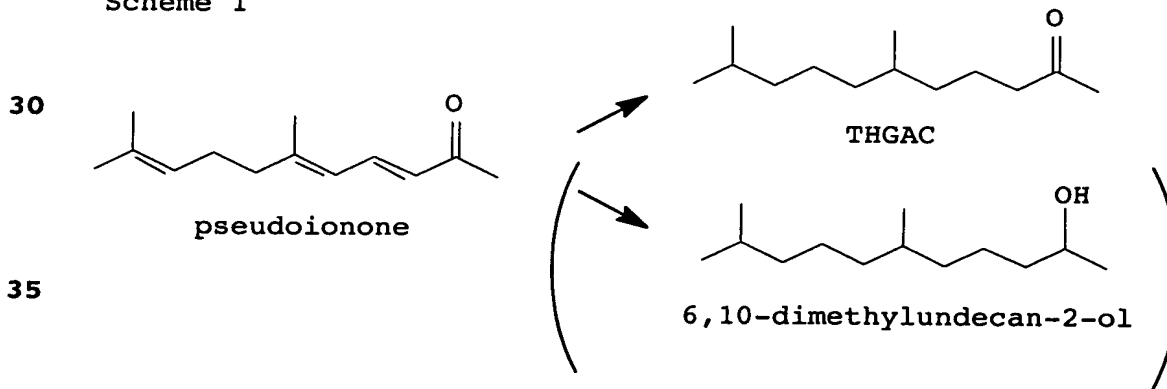
Catalytic hydrogenations over heterogeneous catalysts are in many cases carried out using fixed bed reactors in order to obtain the advantages of continuous process operation. However, specially prepared catalysts have to be produced and used, and when they
5 lose activity, often after only short onstream times, have to be exchanged or regenerated in a costly and inconvenient manner which generally involves not only the shutdown of the hydrogenation plant, but also of the subsequent workup stages.

10 Alternatively, a heterogeneously catalyzed hydrogenation may be carried out in the form of a suspension reaction by suspending the hydrogenation catalyst in a liquid phase with the introduction of mechanical energy, for example in a stirred tank, cf., for example, Ullmanns Encyklopädie der technischen Chemie,
15 4th ed., volume 13, 1997, p. 138, Verlag Chemie Weinheim. An increase in the energy introduced over and above the contribution necessary for suspension does not lead to a significant improvement in the mass transfer of the molecules to be hydrogenated to the surface of the catalyst particles, since the
20 achievable relative velocity between the catalyst particles and the liquid phase only slightly exceeds the sedimentation velocity. Although flow or fluidized bed reactors allow higher relative velocities, they require the use of distinctly larger catalyst particles so that the catalyst bed is more or less
25 extensively expanded in the course of operation. However, the lower surface area relative to volume of relatively large catalyst particles limits the conversion and thus offsets the effect of the higher relative velocity.

30 US 5,939,589 describes a process for carrying out catalytic reactions in which a liquid phase in which a catalyst is suspended and a gas phase in the reactor are conducted through a device which has orifices or channels having a hydraulic diameter of from 0.5 to 20 mm. The hydrogenation of hydrodehydrolinalool
35 to hydrolinalool and further to tetrahydrolinalool is described. Hydrodehydrolinalool contains only one triple bond as a functional group to be hydrogenated, so those skilled in the art would not have discerned any suggestion with regard to selective hydrogenation.
40
It is an object of the present invention to provide a process for preparing THGAC from pseudoionone, geranylacetone and/or dihydrogeranylacetone which has a high selectivity with regard to the hydrogenation of C-C double bonds, i.e. in which the
45 formation of 6,10-dimethylundecanol with reduction of the carbonyl group is substantially suppressed, and which combines

the advantages of a high space-time yield and a simple catalyst
exchange.

We have found that this object is achieved by a process in which
5 pseudoionone, geranylacetone and/or dihydrogeranylacetone,
preferably pseudoionone, in a liquid phase, in which particles of
a catalyst which is capable of preferentially hydrogenating
carbon-carbon double bonds over carbon-oxygen double bonds are
suspended, is conducted through a device which inhibits the
10 transport of the catalyst particles in the presence of a
hydrogen-containing gas.

In the process according to the invention, a relatively high
relative velocity of the liquid phase compared to the catalyst
15 particles is obtained because the transport of the catalyst
particles is inhibited by suitable means such as internals in a
reactor, i.e. the particles are more strongly held back than the
surrounding liquid. In combination with the high surface area
relative to volume of the suspended particles, high space-time
20 yields are achieved as a result.

A suitable device for carrying out the process according to the
invention is described in EP-A 798 039.

25 The device inhibiting the transport of the catalyst particles
preferably has orifices or channels whose hydraulic diameter is
from 2 to 2000 times, in particular from 5 to 500 times, more
preferably from 5 to 100 times, the average diameter of the
catalyst particles.
30
The hydraulic diameter is a measure familiar to those skilled in
the art for describing the equivalent diameter of noncircular
channel structures. The hydraulic diameter of an orifice is
defined as the quotient of 4 times the cross-sectional area of
35 the orifice and its circumference. In the case of channels having
a cross section in the shape of an isosceles triangle, the
hydraulic diameter can be described as

$$\frac{2bh}{b + 2s}$$

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where b is the base, h is the height and s is the congruent
length of the triangle.
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The orifices or channels of suitable devices generally have a hydraulic diameter of from 0.5 to 20 mm, preferably from 1 to 10 mm, more preferably from 1 to 3 mm.

5 Customarily, catalyst particles are used which have an average diameter of from 0.0001 to 2 mm, preferably from 0.001 to 1 mm, more preferably from 0.005 to 0.1 mm.

The device inhibiting the transport of the catalyst particles may 10 comprise a dumped packing, a knit, an open-celled foam structure, preferably made of plastic, for example polyurethane or melamine resin, or ceramic, or a structured packing element, as already known in principle, i.e. by its geometric shape, from distillation and extracton technology. However, for the purposes 15 of the present invention, structured packings in principle have a substantially smaller hydraulic diameter, frequently by a factor of from 2 to 10, than comparable internals in the field of distillation and extraction technology.

20 Useful structured packing elements are in particular metal fabric packings and wire fabric packings, for example of the design Montz A3, Sulzer BX, DX and EX. Instead of metal fabric packings, it is also possible to use structured packings made of other woven, knitted or felted materials. Further useful structured 25 packings are of flat or corrugated sheets, preferably without perforation, or other relatively large orifices, for example corresponding to the designs Montz B1 or Sulzer Mellapak. The structured packings made of expanded metal are also advantageous, for example structured packings of the type Montz BSH. A decisive 30 factor for the suitability of the structured packing for the purposes of the present invention is not its geometry, but the orifice sizes and channel widths in the structured packing which are available for liquid flow.

35 In a preferred embodiment, the surfaces of the device facing toward the liquid phase have a roughness in the range from 0.1 to 10 times, preferably from 0.5 to 5 times, the average diameter of the catalyst particles. Preference is given to materials whose surfaces have an average roughness value R_a (determined according 40 to DIN 4768/1) of from 0.001 to 0.01 mm. When woven stainless steel wire packings are used, an appropriate surface roughness may be achieved by thermal treatment in the presence of oxygen, for example by heat treating the weave under air at a temperature of about 800°C.

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The liquid phase preferably comprises at least 80% by weight, in particular at least 90% by weight, of pseudoionone, i.e. it preferably comprises no significant amounts of diluent. Although not preferred, the liquid phase may comprise diluents, for
5 example C_1-C_4-alkanols, for example methanol.

The hydrogen-containing gas is generally hydrogen gas having a purity of at least 99.5% by volume. It is used in at least a stoichiometric quantity, based on the carbonyl compound present
10 in the liquid phase, usually in an excess of from 1 to 20%.

The catalysts used may be a commercial suspension catalyst which is capable of preferentially hydrogenating carbon-carbon double bonds over carbon-oxygen double bonds. Particularly useful
15 catalyts are those which comprise at least palladium as the active component. In addition to palladium, the catalyst may also comprise further active components, for example zinc, cadmium, platinum, silver or a rare earth metal such as cerium. The catalyst may be used in metallic and/or oxidic form. Preference
20 is given to applying the active components to a support material. Examples of useful support materials include SiO_2, TiO_2, ZrO_2, Al_2O_3 or carbon such as graphite, carbon black or activated carbon. Owing to its easy suspendability, preference is given to activated carbon. The palladium content is preferably from 0.1 to
25 10% by weight, in particular from 0.5 to 7% by weight and more preferably from 2 to 6% by weight, based on the total weight of the catalyst.

The suspended catalyst material may be introduced into the liquid
30 phase and is distributed within it with the aid of conventional techniques.

The device inhibiting the transport of the catalyst particles is customarily a plurality of internals in a reactor which are
35 configured in such a manner that the reaction mixture is forced through the device when it passes through the reactor, i.e. the internals generally fill the entire free cross section of the reactor. The internals preferably, but not necessarily, extend over the entire elongation of the reactor in the flow direction
40 of the liquid phase.

Various reactor forms are suitable, such as jet nozzle reactors, bubble columns or tube bundle reactors. Among these, a particularly suitable reactor is a vertical bubble column or a
45 tube bundle reactor in which the internals are accommodated in the individual tubes.

Preference is given to conducting the hydrogen-containing gas and the liquid phase through the reactor in cocurrent, preferably against the direction of gravity. The gas phase is intimately mixed with the liquid phase, for example, by means of an injector
5 nozzle. The superficial velocity of the liquid phase is preferably not more than 100 m^3/m^2h, in particular from 100 to 250 m^3/m^2h, and that of the gas phase is preferably more than 100 m^3/m^2h (STP), in particular from 100 to 250 m^3/m^2h (STP). In order to achieve sufficiently high superficial velocities,
10 preference is given to recycling substreams of the gas and liquid phases which leave the reactor.

The catalyst particles suspended in the hydrogenation effluent are removed by customary processes, for example by sedimentation,
15 centrifugation, cake filtration or crossflow filtration.

Preference is given to carrying out the process at a pressure of from 1 to 100 bar, more preferably from 1 to 50 bar, and in particular from 1 to 20 bar. The reaction temperature is
20 preferably from 20 to 150°C, more preferably from 20 to 120°C and in particular from 40 to 80°C.

The process according to the invention is illustrated by the appended figures and the example which follows.
25
Figure 1 shows a schematic of a plant which is suitable for carrying out the process according to the invention and comprises a reactor (bubble column) 1 having a structured packing 2 which inhibits the transport of the catalyst particles. Liquid is
30 introduced into the reactor via the line 3 and hydrogen gas via the line 4. The cycle gas 5 is mixed with fresh gas and the suspension 11 circulated by the pump 14 using the mixing nozzle 6. The reactor effluent is transferred via the line 7 into the separating vessel 8 in which the gas phase is separated and
35 removed via line 9. A substream of this gas is withdrawn via line 10 to limit the accumulation of gaseous impurities and the remainder is conducted into the reactor via line 5. The suspended catalyst remains in the reactor system by being held back by a crossflow filter 12 and only catalyst-free liquid phase exits via
40 line 13 and is withdrawn. The heat exchanger 15 can be used to precisely adjust the temperture in the reactor sytem.

Figure 2 shows a schematic of a layer of a corrugated weave. Structured packings usable according to the invention are
45 obtained when two or more of these layers are arranged on top of one another. Each layer comprises channels having a cross section

in the shape of an isosceles triangle having the congruent length
s, the base b and the height h.

Examples

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A plant as described in Fig. 1 was used which comprised a bubble
column (length 1000 mm, diameter 27.3 mm) equipped with a
structured woven packing of the type Montz A3 1200. The
structured packing consisted of layers arranged on top of one
10 another of a stainless steel wire weave which was corrugated in
such a way that channels having a cross section in the shape of
an isosceles triangle were formed which had a congruent length
3.1 mm, base 5.1 mm and height 1.8 mm, corresponding to a
hydraulic diameter of 1.62 mm.
15

Pseudoionone (97% by weight) with the catalyst suspended in it
and hydrogen gas were introduced from below into the packed
reactor in cocurrent at a superficial velocity of 200 $m^3/m^2{*}h$. The
catalyst used was a commercial Pd-carbon suspension catalyst
20 having a palladium content of 5% on activated carbon and an
average particle size of 50 μm.

Example 1

25 The reaction was effected continuously under a hydrogen pressure
of 10 bar and at a temperature of 100°C. A conversion of more than
99.9% was obtained and tetrahydrogeranylacetone was formed with a
selectivity of more than 96%, based on the total amount of
product. The selectivity for 6,10-dimethylundecan-2-ol was 3%.
30 The catalyst hourly space velocity was 2.5 $kg_{pseudoionone}/$
($kg_{catalyst}{*}h$); the space-time yield was 500 $kg_{pseudoionone}/(m^3{*}h)$.

Example 2

35 The reaction was effected continuously under a hydrogen pressure
of 10 bar and at a temperature of 60°C. A conversion of more than
99.9% was obtained and tetrahydrogeranylacetone was formed with a
selectivity of more than 96%, based on the total amount of
product. The selectivity for 6,10-dimethylundecan-2-ol was 0.3%.
40 The catalyst hourly space velocity was 2.5 $kg_{pseudoionone}/$
($kg_{catalyst}{*}h$); the space-time yield was 500 $kg_{pseudoionone}/(m^3{*}h)$.

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